IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

KETTUNEN

Serial No.   09/533,904

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Atty. Ref.:   **10-1304**

Group: **1731**

Examiner: **Nguyen**

For: **COOKING CELLULOSE MATERIAL USING HIGH ALKALI CONCENTRATIONS AND/OR HIGH PH NEAR THE END OF THE COOK**

* * * * * * * * * * *

Honorable Commissioner of Patents
 and Trademarks
Washington, DC 20231

RULE 132 DECLARATION OF AUVO K. KETTUNEN

Sir:

Pursuant to 37 CFR §1.132, the undersigned, **Auvo K. KETTUNEN**, hereby declares and states that:

1.   I am the sole inventor of the subject matter disclosed and claimed in U.S. Patent No. 5,799,856 ("the '856 patent") and its above-identified reissue application.

2.   On information and belief, I understand that the Examiner in the above-identified reissue application has raised an issue with respect to whether or not "cooking" may occur under certain conditions as disclosed in the '856 patent and its above-identified reissue application.

3. "Cooking" of wood chips can occur under various conditions. In this regard, wood chip cooking is a chemical reaction which, like any other chemical reaction, requires three criteria exist, namely: temperature, time and (in the case of wood chip cooking) effective alkali concentration.

4. The three criteria of temperature, time and effective alkali concentration needed to effect wood chip cooking have been well known to those in this art. In this regard, as early as 1965, it was known that, at temperatures below 150°C, at least as low as 140°C, wood chip "cooking" takes place (See, attached copy of Pulping Processes, by Sven A. Rydholm, published 1965, pages 620-621 and 645, the content of which is expressly incorporated hereinto by reference). As work to better understand the chemistry of kraft cooking continued, the study of the criteria necessary for successful processing of wood chips continued. In 1992, the results of a study by Pascale Gouttenoire, Salman Azia and H.S. (Doug) Dugal were presented at the 1992 TAPPI Pulping Conference (See, the attached copy of "Improved MCC Kraft Pulping Using a Lower Temperature Stage", Gouttenoire et al, 1992 TAPPI Conference Proceedings, page 691-697, the entire content of which is expressly incorporated hereinto by refernce). These results indicate pulp produced from cooking the wood chips in a first stage at the low temperature of 120°C was greatly improved over pulp produced when the first cooking stage was conducted at higher temperatures.

5. It is my firm technical belief and understanding, that cooking can and does occur at temperatures of 120° to 160°C such as disclosed in the '856 patent at column 9, lines 30-32 when the two additional criteria of effective alkali concentration and time are present. Thus, when the conditions of the effective alkali concentrations of at least 10g/l as disclosed in the '856 patent column 2, line 67 through column 3, line 3, in conjunction with temperatures of above 120°C and sufficient time of at least five minutes

usually one-half to three hours (see the '856 patent at column 9, lines 32-34) are present, wood chips undergo "cooking", regardless of the name tag that may be given the vessel or the zone within the vessel in which such criteria exist.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted,

JUNE 25 TH 2007
_____
Date Signed

_____
Auvo K. KETTUNEN

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Pulping Processes

SVEN A. RYDHOLM

Research Director
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1965

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solvation of the alkali and therefore easier penetration and reaction of the alkali with the wood constituents.

The effect of the *liquor concentration* has also been shown in the case of *kraft* cooking (459, 516, 707), where in the range 0.5–1.5 M solution the rate constants show a linear dependence on the concentration, Figure 9.110 (459). Normally, however, the charge of cooking chemicals is limited to an amount which only slightly exceeds that consumed in the cook, and the concentration will consequently change throughout the
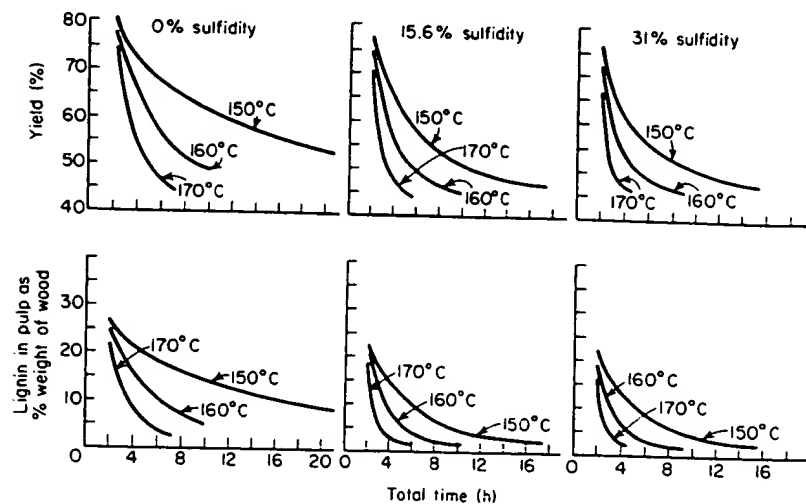
Fig. 9.108. Effect of cooking time, temperature and sulfidity on the rate of kraft cooking of Scandinavian spruce. Heating time 2 h, active alkali charge 242 kg ptw (Hägglund–Hedlund)
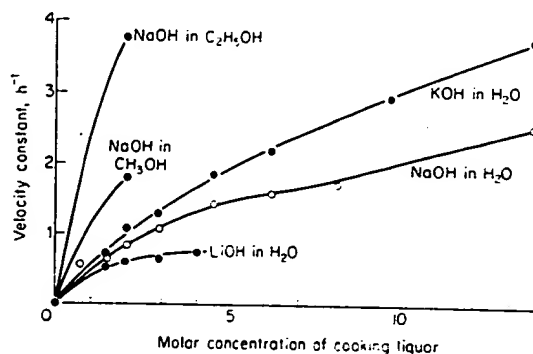
Fig. 9.109. Reaction velocity vs. molar concentration of sodium hydroxide on pulping sprucewood at 160 C (Larocque–Maass)

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cook. The possibility of affecting the rate of pulping by increasing the concentration is in actual practice thus fairly limited, and although additions of excess cooking chemicals are sometimes used to increase the capacity of the digester house, a temperature increase is a more efficient means. However, it has also been found (e.g. 516) that it is desirable to maintain a high chemical concentration by keeping the *liquor-to-wood ratio* at a minimum. A liquor-to-wood ratio of 3:1 will allow a reduction in the alkali charge by 20% in comparison with a cook with the ratio 6:1, to achieve the same degree of delignification (516), or also a corresponding reduction in time or temperature. Figure 9.111 (707) demonstrates that the effects within the normal variations in the liquor-to-wood ratio are not very great, and that an increase in chemical concentration may result in somewhat decreased yields at constant degree of delignification. In batch cooking it is necessary to maintain a certain minimum volume of cooking liquor to achieve a uniform liquor circulation in the digester, normal liquor-to-wood ratios being around 3.5–4.5:1, and black liquor is used for dilution to avoid extra costs in the evaporation plant. Therefore, an initial concentration of 40–60 g/l. NaOH of active alkali in the cooking liquor is normal. Continuous cooking does not require the same liquor ratios, and modern practice involves only white liquor feed to the digester top. This, together with chip moisture and steaming condensate, would constitute about 2.0–3.0 m³ ptw, depending on the moisture content of the chips.

The beneficial effect of *sulfide* in alkaline cooking for both the rate of pulping and pulp quality has been well known since the start of the kraft pulping industry, but the exact amount of sulfide necessary has been a matter of discussion. The question is of both theoretical and
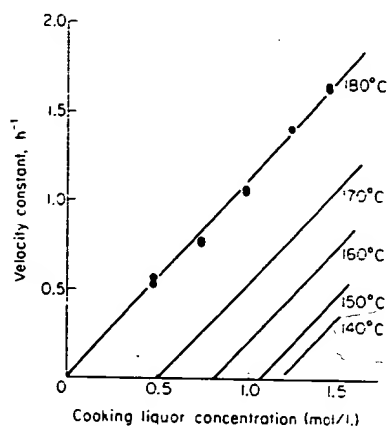

Fig: 9.110. Reaction velocity vs. cooking liquor concentration on the kraft cooking of slash pine at varying temperature (Kulkarni–Nolan)

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details, more or less pronounced in the various wood species, such as fiber dimensions, especially length and wall thickness, summerwood content, etc., will cause large differences in the properties of pulps from various species. However, during the cook, the inherent properties of the fibers are changed to a considerable extent, and therefore the conditions of the cook also influence the final pulp quality. Three main chemical factors are thereby important, as in the case of all paper pulping processes, namely the *degree of delignification*, the *extent of carbohydrate dissolution*, and the *extent of degradation of the remaining carbohydrates*. Also the *location* and *degree of lateral order* of residual hemicelluloses are of importance.

The lignin remaining in the pulp checks the swelling of the fibers on beating, and therefore, the *response to beating* as well as the development of fiber-to-fiber bonds is decreased on increasing the lignin content, as demonstrated in Figures 9.138–139 (429, 479) for spruce and aspen. On prolonged cooking to lower lignin content, the degradation of the carbohydrates becomes noticeable, resulting in a decrease in the tensile and bursting strengths. Therefore there is an optimal degree of cooking, which for normal kraft pulping conditions corresponds to a chlorine number of 5–7 (273e, 324, 429), which is the main level of chemical softwood kraft pulps. Only when special grades are desired, such as unbleached grades of high brightness, is the chlorine number purposely lowered below 4. Pulp for bleaching should be cooked to a degree giving
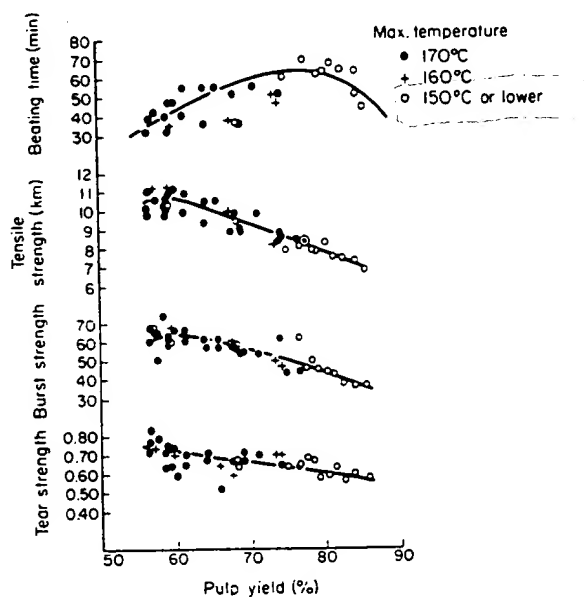

Fig. 9.139. Paper properties of aspen kraft pulp of varying yield, after beating to 300 C.S. (Legg–Hart)

IMPROVED MCC KRAFT PULPING USING A LOWER TEMPERATURE STAGE

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ABSTRACT

Extended delignification of southern pine wood chips, using an improved modified continuous cooking (IMCC) process was investigated. It is common practice to conduct modified continuous cooking (MCC) trials with both stages at 170°C.

In this study, the MCC process was further improved by cooking the first stage at a much lower temperature of 120°C and the second stage at 170°C. The lower temperature in the first stage was used to minimize degradation of carbohydrates. The optimum split ratio of effective alkali under these conditions was 50/50, resulting in 2% higher pulp yield, improved viscosity and strength properties similar to the control.

Addition of a catalyst, anthraquinone (AQ), to the second stage showed no improvement in delignification efficiency. Further studies need to be done to quantify the effect of catalysts.

INTRODUCTION

One way of decreasing the pollution load caused by bleaching of chemical pulp is to reduce the lignin content of the pulp prior to bleaching. Several approaches such as extended delignification, the addition of catalysts (AQ, polysulfide), or chemical treatment of chips (sulfide solutions) can be used to improve delignification in the pulping stage. Further reduction of lignin can be achieved with oxygen delignification or other treatment processes (e.g., enzymes).

Extended delignification in the pulping digester (batch & continuous) has been studied by several researchers. The process involves modifying the liquor streams during kraft pulping to optimize pulp yield and increase delignification. Three important conditions known to minimize loss of pulp strength (1-5) are listed below.

1) Effective alkali concentration should be lowered initially and kept relatively uniform throughout the cook to retain both yield and viscosity.

2) Hydrogen sulfide ion (HS⁻) concentration should be as high as possible (40% sulfidity), especially during initial delignification and the first part of the bulk delignification phase.

3) The amount of dissolved lignin in the pulping liquor should be kept low, especially during the final phase of the cook, to avoid an adverse effect on the carbohydrate selectivity.

Thus, under these conditions, a normal Kappa number of 32-35 can be decreased to 22-25 while retaining the same pulp properties and reducing bleach consumption of active chlorine by 20%.

In previous studies, either with a continuous digester (6-8) or a batch digester (9-10), MCC cooks were conducted at 170°C in both stages. Most of the reactions on carbohydrates (peeling and hydrolysis) occurred during the initial stage before maximum temperature was reached, as the kinetics of carbohydrate dissolution depends not only on the alkalinity of the cook but also on the reaction temperature (11). In order to minimize those unavoidable reactions in this study, kraft cooks were conducted at a lower first stage temperature of 120°C, followed by the second stage at 170°C. To decrease the high sulfide load (60%), some experiments were also conducted using anthraquinone.

EXPERIMENTAL

Air-dried loblolly pine (Pinus taeda) chips were used in a six-liter batch digester equipped with a pump for liquor circulation. Chip charge was 500 g o.d.; liquor-to-wood ratio was 4:1.

For IMCC and MCC processes, half of the black liquor (1 liter) was removed from the bottom of the digester and replaced with 1 liter of preheated white liquor transferred from a similar digester. The fresh liquor was preheated in order to obtain the correct temperature after the transfer.

At the end of the cook, the liquor was cooled to 70°C with an indirect water cooling system before opening the digester. Chips were fiberized in a William Stirer. The pulp was screened through a 0.25 mm flat screen and air dried. Screened pulp was beaten in a PFI mill for 4500 and 6500 revolutions and tested according to TAPPI standard methods.

Effective alkali and sulfidity were chosen according to previous studies on batch digesters (2, 3, 10) and kept the same for all cooks: EA=16% Na₂O and S=40%. The effective alkali split ratio was varied, i.e., the split in percent of effective alkali charged at the start of the cook and at the time of liquor displacement. Three split ratios were studied: 70/30, 60/40 and 50/50 to keep the soda concentration as equal as possible throughout the cook. (Respective soda concentrations are given in Table I.) Kinetics were conducted at 120°C, then 170°C, and compared with the controls [conventional and modified continuous cooks at 170°C (Tables I and II)]. Data for the two cooks include the split ratio and temperature of the two stages.

Table I. Soda concentrations at the beginning of the two stages for the different split ratio.

	1st Stage	2nd Stage
Conventional Cook	0.97N	
IMCC 70/30	0.68N	0.42N
IMCC 60/40	0.58N	0.47N
IMCC 50/50	0.48N	0.52N

Table II. Pulping conditions for conventional and modified cooks.

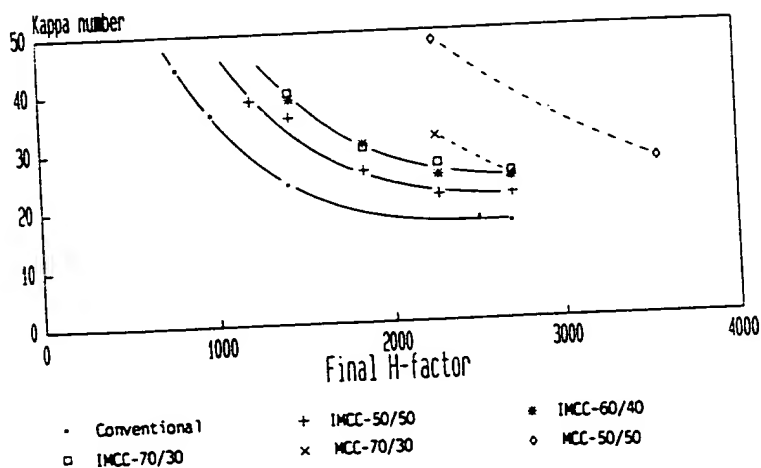|	Conven-tional	IMCC Stages		MCC Stages	
		1st	2nd	1st	2nd
Time to Max. Temp. (min.)	90	60	30	90	0
Max. Temp. C.	170	120	170	170	170
Time at Max. Temp. (min.)	50-180	60	90-180	60	90-180
Final H-factor	790-2700	1200-2700		2300-3500	

RESULTS AND DISCUSSION

As the rate of pulping reaction (kinetics) is determined by OH and HS concentrations in the liquor throughout the cook, modified processes are always longer in duration than conventional cooks (because of the lower soda concentrations shown in Table I). For this reason, as shown in Figure 1, the rate of reaction of the 50/50-IMCC is faster than both the 70/30 and 60/40-IMCC. During the first stage at 120°C, a very small part of the lignin is dissolved and the bulk of the delignification takes place during the second stage. Thus, 50/50-IMCC is favorable, providing more alkali during the second stage. For the MCC, it is the opposite; as the bulk delignification begins during the first stage, the 70/30 split ratio is favorable.

Figure 1. Delignification kinetics of the different processes.

- Conventional
- □ IMCC-70/30
- + IMCC-50/50
- × MCC-70/30
- * IMCC-60/40
- ◇ MCC-50/50

It is interesting to note that the rate of delignification of the IMCC is faster than 70/30-MCC, e.g., a Kappa number of 25 needs a 1900 H-factor to be reached with 50/50-IMCC versus a 2700 H-factor for 70/30-MCC. Thus, a first stage at 120°C ought to improve chip impregnation and lignin dissolution during the bulk delignification. It is also possible that a shortage of alkali during the MCC reaction results in lignin redeposition onto the chips.

Differences are also shown for soda consumption (Figure 2). More alkali is consumed during the 50/50-IMCC than 60/40 and 70/30-IMCC. For IMCC, soda consumption stays the same during the reaction kinetics and increases at the end when no delignification is occurring but when yield and viscosity are decreasing (Figures 3 and 4). Conventional soda consumption increases gradually during delignification to about the same value as that for 50/50-IMCC. Soda consumption is higher for the MCC process with a lower rate of delignification. This can happen through increased reactions with carbohydrates or other noncellulosic material during the first stages at high temperature.

Figure 2. Total NaOH consumed throughout the delignification kinetics for the different processes.

| • Conventional 170 | + IMCC-50/50 | ✳ IMCC-60/40 |
| □ IMCC-70/30 | ··×·· MCC-70/30 | ··◇·· MCC-50/50 |

Figure 3. The screened yield vs. kappa number for the different processes.

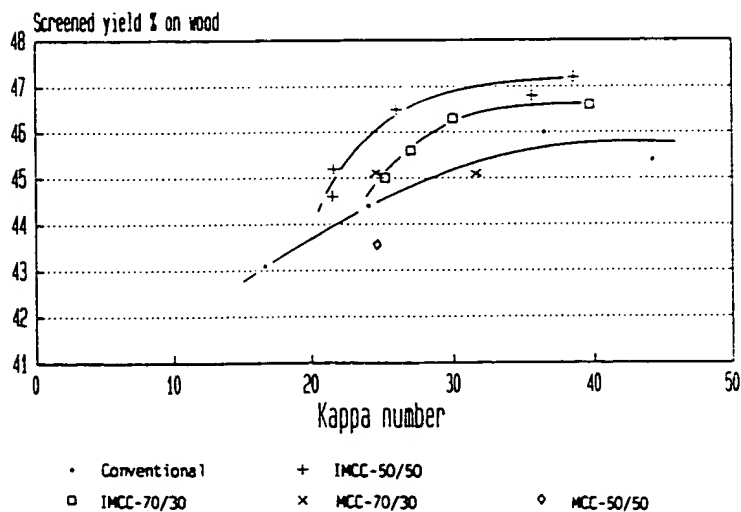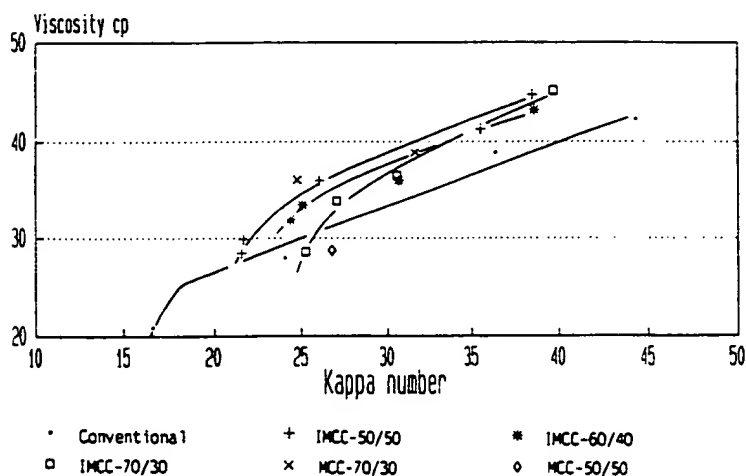| • Conventional | + IMCC-50/50 | |
| □ IMCC-70/30 | × MCC-70/30 | ◇ MCC-50/50 |

Figure 4. Viscosities *vs.* kappa number for the
different processes.

Study of the screened yields and viscosities also show a positive effect of the IMCC process (Figures 3 and 4). At constant Kappa number, the screened yield is higher for the IMCC process, especially with the 50/50 split ratio. At a 25 Kappa number, the screened yield is about 2 percentage points higher than for a conventional cook. (MCC processes are also lower in yield than the IMCC processes.) A similar pattern is obtained for pulp viscosities (Figure 4).

The chemical composition of the pulp (Table III) does not show significant differences between the pulps, according to a previous study (10). Optical microscopy confirms no differences in fiber lengths. Physical properties also confirm that the fibers are not affected during the IMCC process. In spite of a slightly easier beating capacity of the conventional pulps, tear and burst indexes are higher with the 50/50-IMCC process (Figures 5 and 6).

Figure 5. Tear index *vs.* burst index for pulps with
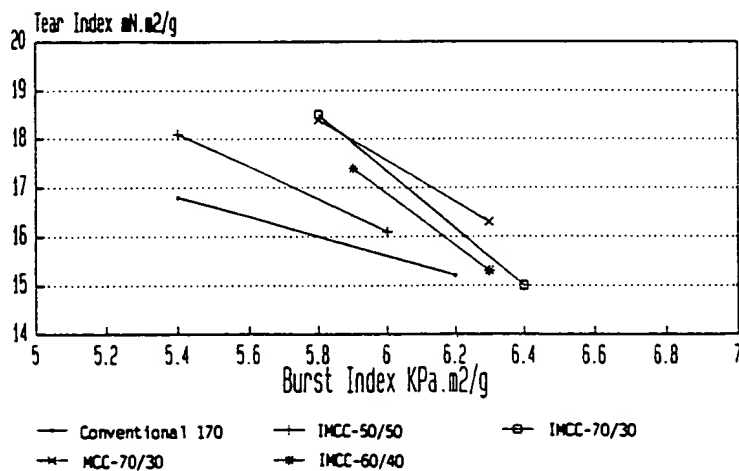kappa number ca. 25, at 4500 and 6500 PFI
revolutions.

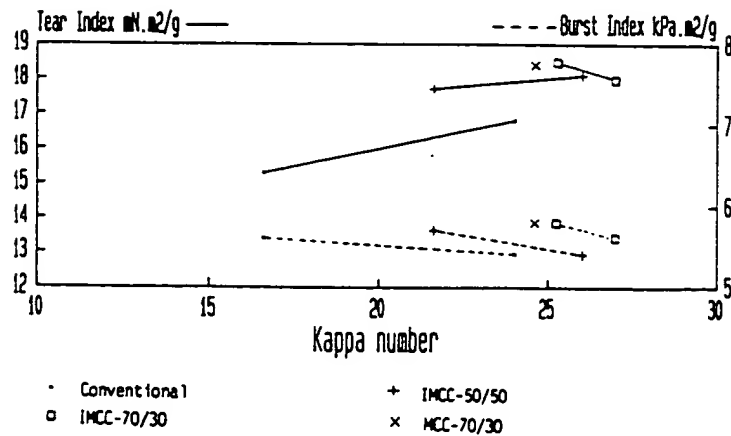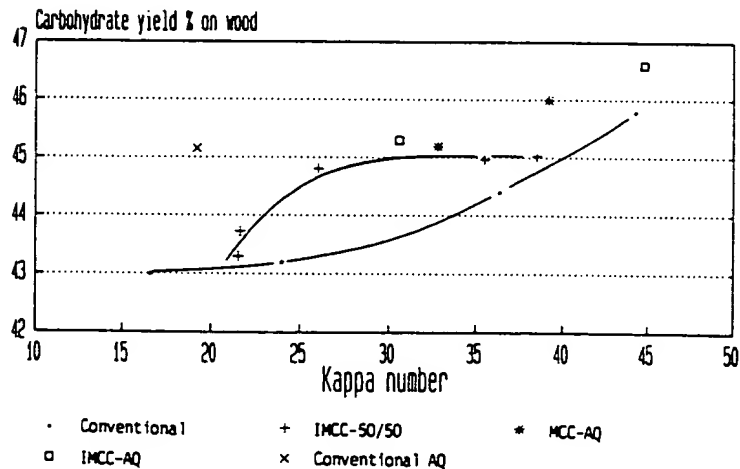Figure 6. Tear and burst indexes vs. kappa number at
4500 PFI revolutions.

Tear Index mN.m2/g ——   - - - -Burst Index kPa.m2/g

- Conventional   + IMCC-50/50
□ IMCC-70/30   × MCC-70/30

Table III. Chemical composition of pulps.

	Conventional		IMCC 50/50		IMCC 70/30
Kappa Number	24	16.6	26	21.6	27
Arabinan*	0.7	0.6	1.0	0.6	0.6
Xylan*	7.8	7.6	7.0	7.6	7.4
Mannan*	7.5	8.0	8.9	7.8	7.6
Galactan*	0.4	0.1	0.8	0.1	0.1
Glucan*	80.3	79.4	78.6	78.5	76.3
Lignin*	3.6	2.8	4.5	3.9	4.2

*% in pulp o.d. at 105°C

With IMCC process, the first stage at 120°C provides better liquor impregnation and less peeling reaction of the carbohydrates than the conventional MCC process. Soda reacts more with lignin and thus improves the delignification in the 170°C stage. However, it is important to note that toward the end of the delignification, the carbohydrates rapidly dissolve as more soda is consumed (Figure 7). This means that the delignification selectivity decreases and is similar to the conventional process. The screened yield is better with the IMCC process and the middle lamella is more delignified. It would be interesting to follow the kinetics by UV microscopy to confirm if there is a slight modification of the delignification topochemistry with an initial middle lamella dissolution and a later S_2 cell wall attack with reactions on the LCC.

Figure 7. Carbohydrate yield vs. kappa number.
Carbohydrate yield = (100-0.15 kappa number)
x total yield.

Carbohydrate yield % on wood

- Conventional   + IMCC-50/50   * MCC-AQ
□ IMCC-AQ   × Conventional AQ

IMCC PROCESS WITH AQ

Some attempts were made to replace a part of the sodium sulfide by AQ (conditions in Table IV). According to Kutney (12), for southern pine, 0.1% AQ can replace 10.2% sulfide. Previous studies on MCC processes have shown that sodium sulfide is especially important during the initial phase and the beginning of the bulk delignifications. Therefore, sulfide was partly replaced by AQ during the second stage of the IMCC process and added with the preheated white liquor. All cooks were conducted to 1860 H factor at the same conditions used for the best results obtained with the 50/50-IMCC process (K=26, viscosity=36 cp). In comparison, results show that cooks with AQ in the second stage have a higher Kappa number and lower viscosity (Table V) but the carbohydrate yield is not lower (Figure 7). The best results are obtained for the conventional process with AQ which has a rate of delignification similar to the conventional kraft process but with a much higher carbohydrate yield. The results may suggest that AQ is less effective as a catalyst when added at the second stage during the bulk delignification. It is more effective when added before the bulk delignification (Pulp 4). Thus, it seems that when soda has reacted with wood, AQ is no longer efficient and there is a kind of competition between the two. This result is also reported by Robert, et al. (13, 14) who found that, when AQ is added during the second stage of a cook (a different process than MCC), AQ is not efficient, and when soda concentration is increased in the cell wall, AQ is less effective. The proposed explanation would be that both react with the β-0-4 bonding of the lignin carbohydrate components (LCC) and not Na_2S.

Table IV. Conditions for cooks with anthraquinone.

Pulp Number	NaOH % EA	Na2S %EA	AQ %O.W.	Temp. °C	Time at Max. Temp., min.
1 Conventional	14	2	0.3	70	120
2 1st stage	8.4	2.8	---	170	60
2nd stage	3.6	---	0.3	170	60
3 1st stage	8.4	2.8	---	170	60
2nd stage	4.8	---	0.3	170	60
4 1st stage	6	2	---	120	60
2nd stage	6	---	0.3	170	120
5 1st stage	6	2	---	120	60
2nd stage	8	---	0.3	170	120

Table V. Results of IMCC-anthraquinone cooks.

Pulp Number	1	2	3	4	5
NaOH Consumed, %O.W.	11.0	10.3	10.7	11.0	12.1
Na2S Consumed, %O.W.	3.8	5.5	5.4	4.1	4.0
Screened Yield, %O.W.	46.3	46.2	46.7	47.2	46.4
Total Yield, %O.W.	46.5	48.9	47.6	50.0	47.5
Kappa Number	19.2	39.2	32.8	44.8	30.6
Viscosity, cp	22.7	37.0	35.0	33.0	25.9

CONCLUSIONS

The following conclusions can be drawn from this study.

1. For pulps with a Kappa number of 25, laboratory results indicate that IMCC with a first stage at a lower temperature (120°C) provided better results than cooks with two stages at 170°C.

2. The reaction kinetics were faster for IMCC with a split ratio of 50/50 than for the split ratio 60/40 and 70/30, yield was 2% higher and viscosity also improved when compared with the conventional process.

3. Strength properties from an IMCC pulp at Kappa 26 were similar to those of conventional pulps but had higher pulp yields.

4. Trials with AQ were not successful. AQ added during the second stage (to replace Na_2S) was shown to be inefficient in enhancing delignification. When the AQ trials were compared with the IMCC split ratio of 50/50, the rate of delignification decreased. If it is really possible to minimize the sodium sulfide load by using AQ, the solution may be to add AQ in both stages. Further investigation needs to be done to verify this theory.

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